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#11

Applicants: **Liao et al.**

Case: **761P7**

Serial No.: **08/825,360** Filed: **March 28, 1997**

Group Art Unit: **2814**

Examiner: **T. Quach**

Title: **AN INTERCONNECT STRUCTURE FOR USE IN AN INTEGRATED CIRCUIT**

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S I R:

DECLARATION UNDER 37 CFR 1.131

We, Marvin Liao, Chyi S. Chern, Jennifer Tseng, Michal Danek, Roderick C. Mosely, Karl Littau, and Ivo Raaijmakers, hereby declare as follows:

1. We are the applicants of the above-captioned patent application.

2. The invention which forms the subject matter of the above-captioned patent application was conceived of and reduced to practice on or before November 8, 1995.

3. Exhibit A is enclosed herewith in support of declaration that we conceived of and reduced to practice the invention in this country on or before November 8, 1995.

S/N 08/825,

4. Exhibit A is an excerpt from a Sematech final report that was submitted by Karl Littau, on or before November 8, 1995, entitled "Low Temperature Chemical Vapor Deposition (CVD) of Titanium Nitride (TiN) with Applied Materials".

5. Section 4.8.2 of Exhibit A (p.27) describes Auger electron spectroscopy data obtained for 50Å and 100Å CVD TiN films deposited upon 300Å PVD titanium (Ti) on silicon (Si) substrates. (See Figures 25-26; pp.28-29.)

6. Exhibit A is offered as supporting evidence that a Ti/TiN film stack comprising TiN layer of less than about 130Å thick was formed by the method of the present invention on or before November 8, 1995, the filing date of the U.S. patent 5,714,418, issued to Bai and Fraser.

The undersigned, Marvin Liao, Chyi S. Chern, Jennifer Tseng, Michal Danek, Roderick C. Mosely, Karl Littau, and Ivo Raaijmakers, hereby declare that all statements made herein of our own knowledge are true and that these statements made on information and belief are believed to be true and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent resulting therefrom.

Date	Marvin Liao

S/N 08/825,[redacted]

Date	Chyi S. Chern
10-15-99 Date	Jennifer Tseng
Date	Michal Danek
10-15-99 Date	Roderick C. Mosely
10-15-99 Date	Karl Littau
Date	Ivo Raaijmakers

SEMATECH

Low Temperature Chemical Vapor Deposition (CVD) Titanium Nitride (TiN) with Applied Materials: J132 Final Report

SEMATECH Confidential

Technology Transfer 94112614A-ENG

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1 EXECUTIVE SUMMARY

This document is the final report on project J132 with Applied Materials to develop and demonstrate a low temperature chemical vapor deposition (CVD) titanium nitride (TiN) technology for use as a barrier material for 0.35 µm and 0.25 µm generation technologies. Specifically, this document addresses the results of the second design of experiments (DOE), second and third passive data collections (PDCs), and process marathon activities. The document also discusses barrier properties of the film and provides recommendations for future work.

An Applied Materials 200 mm P5000 deposition system has been dedicated to CVD TiN technology development. A response surface methodology (RSM) design of experiments enabled a full mapping of the process parameter space and a determination of the sensitivity of the process to changes in the input variables. The most important factors affecting deposition rate were susceptor temperature, TDMAT bubbler temperature, and gas flow rates, with strong interactions between the susceptor temperature and the other main factors. For thickness uniformity, susceptor temperature and gas flow rates were the dominant factors. The film step coverage in high aspect ratio contacts was characterized, and the important factors were identified. A lower temperature resulted in better step coverage; however, excellent step coverage, ≥ 50%, could be achieved even at high temperatures by varying the bubbler temperature and gas flows. Deposition rate, step coverage, and thickness uniformity were optimized, resulting in a process of record. The technology metrics, goals, and end-of-project status are summarized in Table 1.

Table 1 Summary of J132 Metrics, Goals, and Results for CVD TiN

Table Metrics	Goals	End-of-Project Status	Comments
Step Coverage	≥50%	≥70%	As determined by cross-sectional SEMs
Via Resistance	≤Sputtered	≈Sputtered	Based on member company comparison data: integration specific
Contact Resistance	≥Sputtered	≈Sputtered	Based on member company comparison data: integration specific
Defect Density (≥0.2 µm)	≤260/m^2	≈340/m^2	Background: 200/m^2
Cost of Ownership	≤$4.00/wafer	<$4.00/wafer	Stand-alone process
Throughput	≥27 wph	≈25 wph	
Availability	≥85%	91%	Based on marathon data

Particle performance during PDC #2 was essentially within the project goals. Wafer-to-wafer repeatability of the film thickness was above acceptable levels and was investigated further in PDC #3. The wafer-to-wafer thickness repeatability remained high after a chamber idle period but improved if the chamber ran continuously.

A 3000-wafer process marathon showed excellent particle performance over the entire experiment. The film thickness steadily decreased throughout the marathon and was attributed to

a buildup on the edge of the susceptor. A susceptor design modification has been proposed as a solution.

The barrier properties of this film for tungsten plug or aluminum applications are reported. The barrier performance of CVD TiN films depends on the film thickness and was found to be comparable to that for PVD TiN films.

Significant progress has been made in characterizing the capabilities of the technology and addressing areas needing improvement. The model of the full process window has been developed. Particle performance indicates that this technology will meet or exceed all the requirements for 0.25 µm generation technologies

2 INTRODUCTION

Titanium nitride (TiN) is used at contact and via levels as a barrier and adhesion material beneath the subsequent deposition of plug material, e.g., chemical vapor deposition (CVD) tungsten (W). For high aspect ratio (≥ 3:1) contact and via holes, it is technologically difficult and potentially more costly to deposit a continuous, pinhole free barrier with existing physical vapor deposition (PVD) TiN processes.

CVD TiN using either organic or inorganic precursors is an alternative to PVD. A number of CVD TiN processes have been studied extensively. One widely studied inorganic approach is using titanium tetrachloride ($TiCl_4$) as the precursor. The temperature needed for this process (>500°C), however, is deemed too high for many applications. To achieve the high step coverage of a CVD process, metal organic precursors are employed.

Applied Materials strives to develop a production-worthy process and tool for CVD of TiN at low temperatures (wafer temperature ≤ 400°C). This report includes the activity over the final two-thirds of the project and the data to support the technology development. The interim report (Technology Transfer #94062389A-ENG) discussed the initial PDC and DOE work during this project.

2.1 Assumptions

The precursor used in this technology is tetrakis (dimethylamino) titanium (TDMAT, $Ti[N(CH_3)_2]_4$). TDMAT is mixed with other gases, which, in combination, react on the heated wafer surface to decompose into TiN and organic byproducts. The reaction is thermally driven; therefore, no material deposits on any of the cold-wall reactor walls.

The reactor used for these experiments is an Applied Materials 200 mm P5000. The chamber hardware is similar to the Applied Materials lamp-heated WCVD chamber, with minor modifications for chemical delivery. The chamber and process are compatitble with the Applied Materials Endura 5500 and Centura platforms.

3 PROJECT DESCRIPTION

This project includes executing design of experiments (DOE), passive data collections (PDC), and marathon-like activities on a 200 mm Applied Materials CVD TiN deposition system. This is the final report on the technology development.

4.8.2 Barrier to WF_6

To assess the performance of CVD TiN as a barrier to attack from WF_6, a series of CVD TiN films were deposited on top of 300 Å PVD Ti on Si substrates. After CVD TiN deposition, the films were exposed to pure WF_6 for 30 seconds. No co-reactants such as SiH_4 or H_2 were present, thereby preventing deposition of tungsten and allowing the WF_6 to continue to attack the TiN film. These films were then analyzed with Auger electron spectroscopy (AES) to determine the extent of F penetration into the stack. AES spectra for 50 Å and 100 Å CVD TiN films are shown in Figures 25 and 26. With the 50 Å film, there is close to 15% F at the TiN/Ti interface. In the 100 Å CVD TiN spectrum, the F signal was expanded 10X for visualization, showing a maximum F concentration at the interface of 2%. While there is currently no clear understanding of what levels of F in a film affects device performance or yield, these results indicate a lower limit in the film thickness required to maintain an effective barrier to F penetration.

5 CONCLUSIONS

Utilizing DOE techniques, the process window for CVD TiN has been characterized on the Applied Materials P5000. Conformal step coverage in 3.5:1 aspect ratio is >50%, with step coverage of up to 90% achievable. Deposition rates in excess of 400 Å/min are possible across the entire temperature window. Thickness non-uniformity is better than 10% 3σ across a 200 mm wafer.

Particle performance, as demonstrated over a 3000-wafer marathon, is compatible with the requirements for 0.25 µm generation technologies. Barrier performance of the CVD TiN film was found to be compatible to that of PVD TiN films. This CVD TiN process can be used with either W plug or Al technologies.

6 RECOMMENDATIONS/FUTURE PLANS

At the conclusion of this project, a number of issues remained unresolved. These issues fall into two categories: 1) issues pertinent to a manufacturing environment, and 2) issues inherent to the film and TDMAT technology. Excellent particle performance over one 3000-wafer marathon was achieved. However, extending beyond 3000 wafers between chamber cleans while adhering to uniformity, deposition rate, and particle specifications requires additional improvement work.

The viability of a modified susceptor design to eliminate a drop in deposition rate needs to be demonstrated. Longer tests are needed to accurately assess the tool reliability, and multiple cycles of chamber cleans need to be run to assess tool utilization capability and PM frequency.

For certain applications, a reduction in the resistivity of the film is desired and will be the subject of ongoing work at Applied Materials. Understanding of the technology and process through analysis of the conductivity mechanism may also lead to improvements in the film properties. Finally, application-specific issues involving the integrated process flow should be addressed. The interactions between via or contact etch, Ti deposition, and W or Al plug formation need to be better understood.

Both the technology and manufacturing issues could well be addressed in a follow-on program.

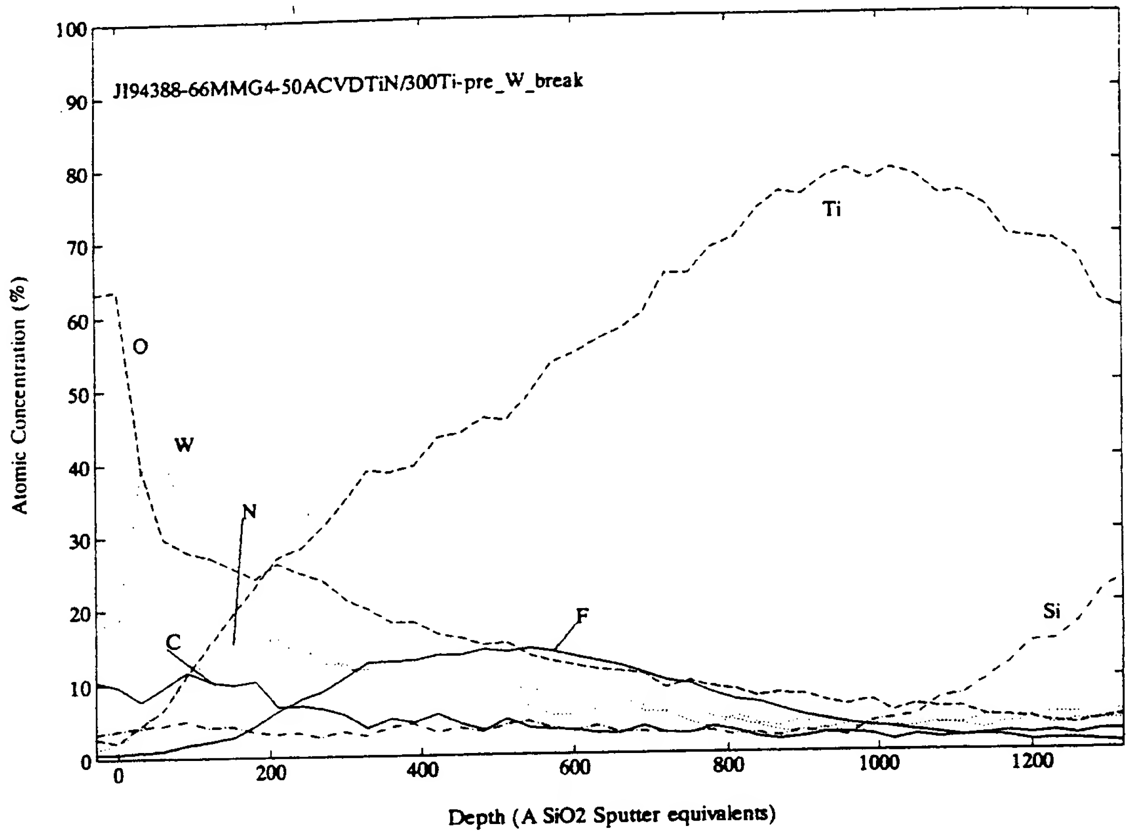

Figure 25 **AES Depth Profile - 50Å CVD TiN Film**

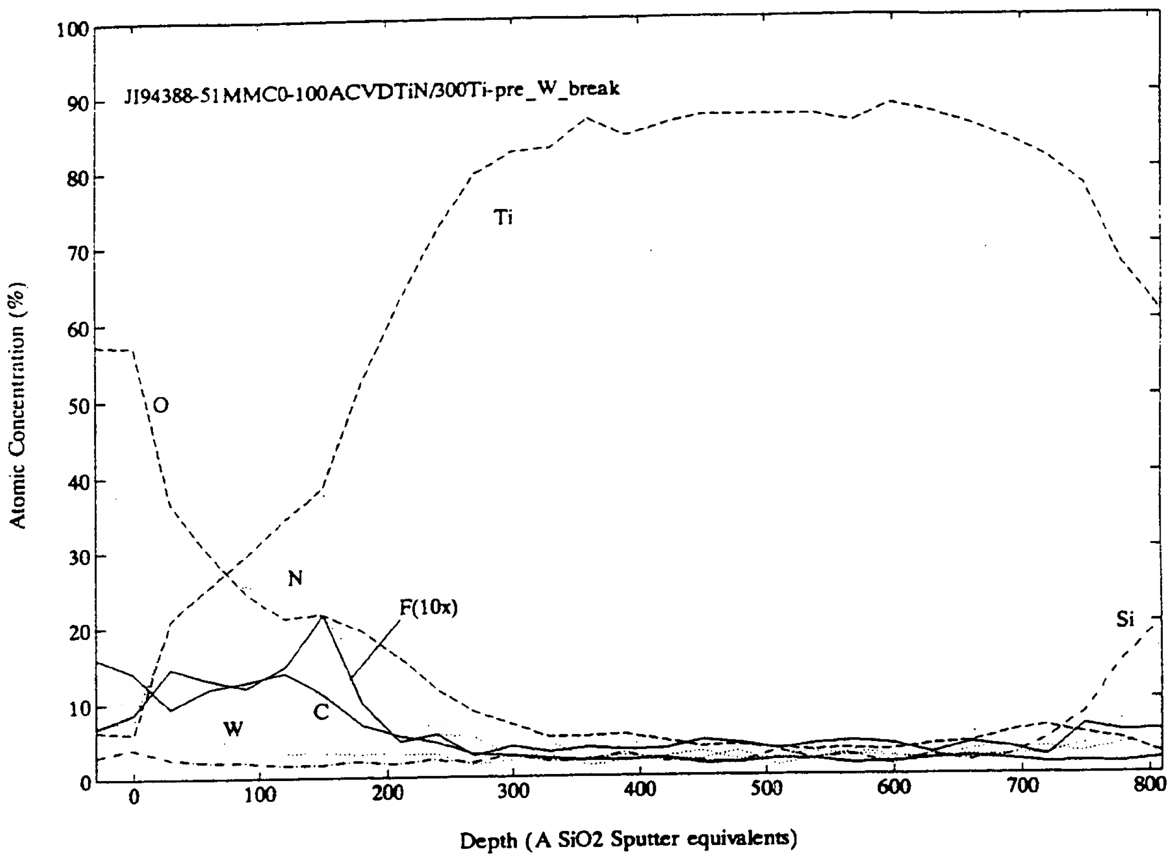

Figure 26 AES Depth Profile - 100 Å CVD TiN Film